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CHEMICAL COMPOSITION OF COMMERCIAL ASPHALT CEMENT AS DETERMINED BY HIGH PRESSURE LIQUID CHROMATOGRAPHY

Prepared for the

STATE OF MONTANA

DEPARTMENT OF HIGHWAYS

In cooperation with the

U.S. DEPARTMENT OF TRANSPORTATION

FEDERAL HIGHWAY ADMINISTRATION

December 1977

by

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16. Abstract

The chemical composition of asphalt cement will determine its quality, which in turn will ultimately influence the performance of bituminous roadways. This investigation was conducted to determine if the chemical composition of asphalts as measured by high pressure liquid chromatography (HPLC) could be used to determine the significant differences between asphalts from good and bad roads. If so, perhaps this method could be used in a predictive manner for improved asphalt specification requirements.

HPLC analysis of asphalt cements from roadways which varied in quality from good to bad showed highly significant differences. Using these differences, these roadways were classified into good, fair, poor and bad. Coupling these data with the relative amounts of asphalt sub-fractions and physical tests such as penetration at 77° F and ductility at 40° F, a reasonable explanation for why a given roadway had reduced performance was established.

Using HPLC analysis and sub-fraction quantities, a qualified prediction on the asphalt quality used in two newly constructed roadways has been advanced.

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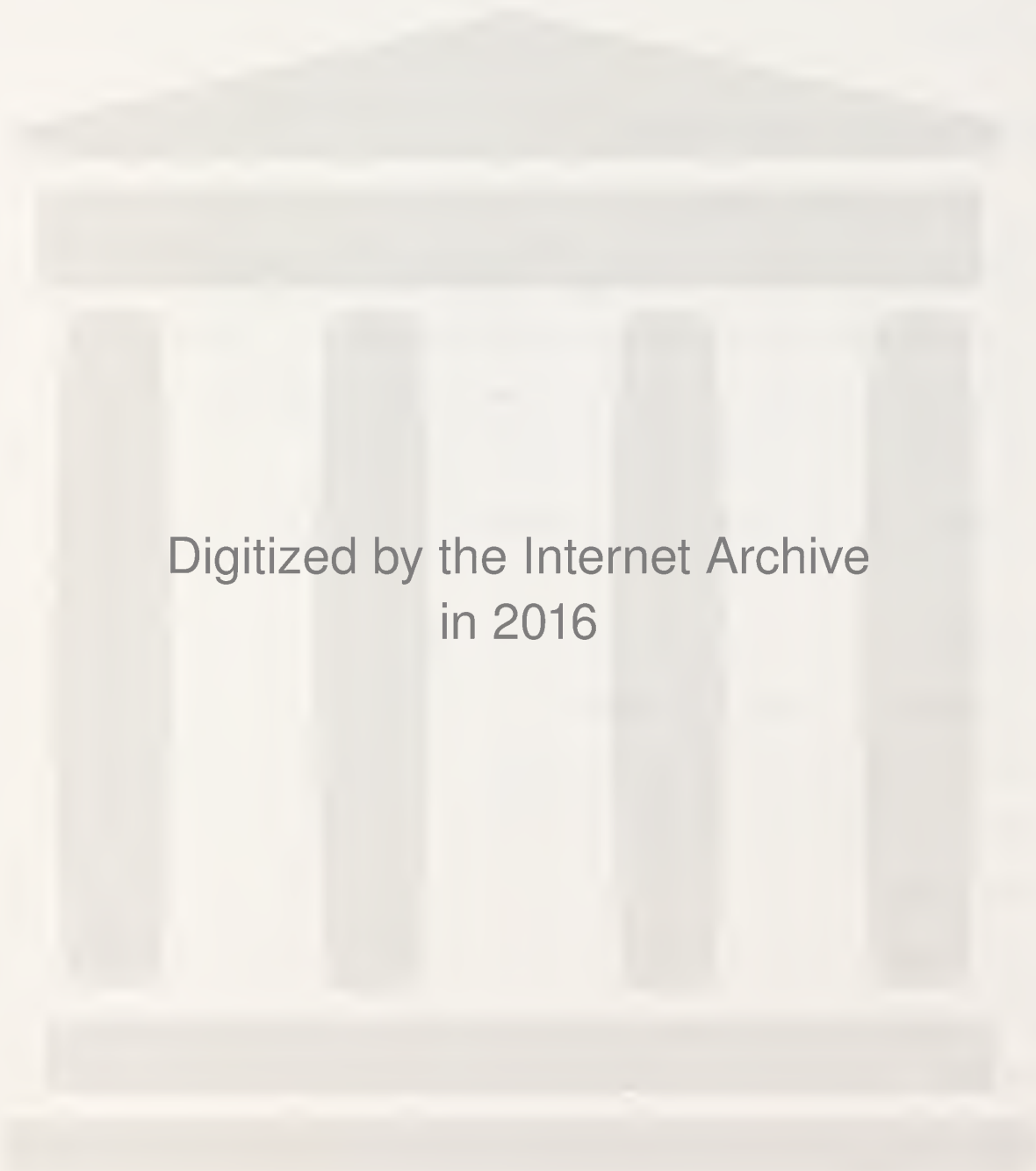
TABLE OF CONTENTS

TITLE	PAGE
DISCLAIMER STATEMENT	i
ABSTRACT	1
INTRODUCTION	2
DISCUSSION OF THE HPLC METHOD	4
ANALYSIS OF VARIOUS ASPHALTS	
Established Roads - 100/120 Penetration Design	7
Established Roads - 120/150 Penetration Design	18
Established Roads - 150/200 Penetration Design	18
New Roads - 120/150 Penetration Design	21
Effects of the Hot Mixing Process on Asphalt	30
EXPERIMENTAL	33
Isolation of Asphalt Cement	33
Fractionation of Asphalt Cement	33
HPLC Analysis of Asphalt Cement	35
Materials	35
CONCLUSIONS	36
IMPLEMENTATION	37
REFERENCES	38
APPENDIX	40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Abstract

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HPLC analysis of asphalt cements from roadways which varied in quality from good to bad showed highly significant differences. Using these differences, these roadways were able to be classified into good, fair, poor, and bad. Coupling these data with the relative amounts of asphalt sub-fractions and physical tests such as penetration at 77° F and ductility at 40° F, a reasonable explanation for why a given roadway had reduced performance was established.

Using HPLC analysis and sub-fraction quantities, a qualified prediction on the asphalt quality used in two newly constructed roadways has been advanced.

Introduction

Several factors are responsible for the overall performance of a bituminous roadway. The major ones appear to be subgrade and base course quality, environment, construction quality, aggregate, asphalt quality, age of road and traffic load. A perturbation applied to any one of these factors will alter the dynamic interaction of all. The quality of asphalt was chosen for study in order to better understand its role in asphalt pavement performance. It is its chemical composition which will determine its capability to interact properly with the other factors. Thus, measurements of chemical composition and interpretation of results should ultimately influence bituminous pavement performance.

Physical tests of asphalt cement such as ductility, penetration and viscosity are indirect measurements of chemical composition. They are measures of colligative properties. It is well-known that asphalt cements from a variety of sources and presumably with differing chemical compositions can meet the specifications required by these physical tests (1). Thus, it is essential to develop tests which more adequately measure the chemical composition of asphalt.

Fractionation of asphalt into smaller groups, sub-fractions, has been shown to provide a more direct measurement of chemical composition (2,3,4) than physical tests. One may use the quantities of these sub-fractions as a fingerprint of a given asphalt sample.

As it is impractical, if not impossible, to determine the amount and character of each chemical component in asphalt, a method was needed which was both practical and an improvement

over existing methods. Therefore, the method of high pressure liquid chromatography (HPLC) was chosen which would provide a measure of the various molecular sizes of any given asphalt sample. It was believed that the size of chemical components would be a factor in asphalt characteristics such as flexibility, volatility and possibly even aggregate asphalt interaction. Furthermore, the molecular size distribution within each of the sub-fractions would improve the interpretation of fingerprints of asphalts. Finally, the method was relatively fast, requiring no more than 5-40 minutes for each determination.

The immediate objectives were:

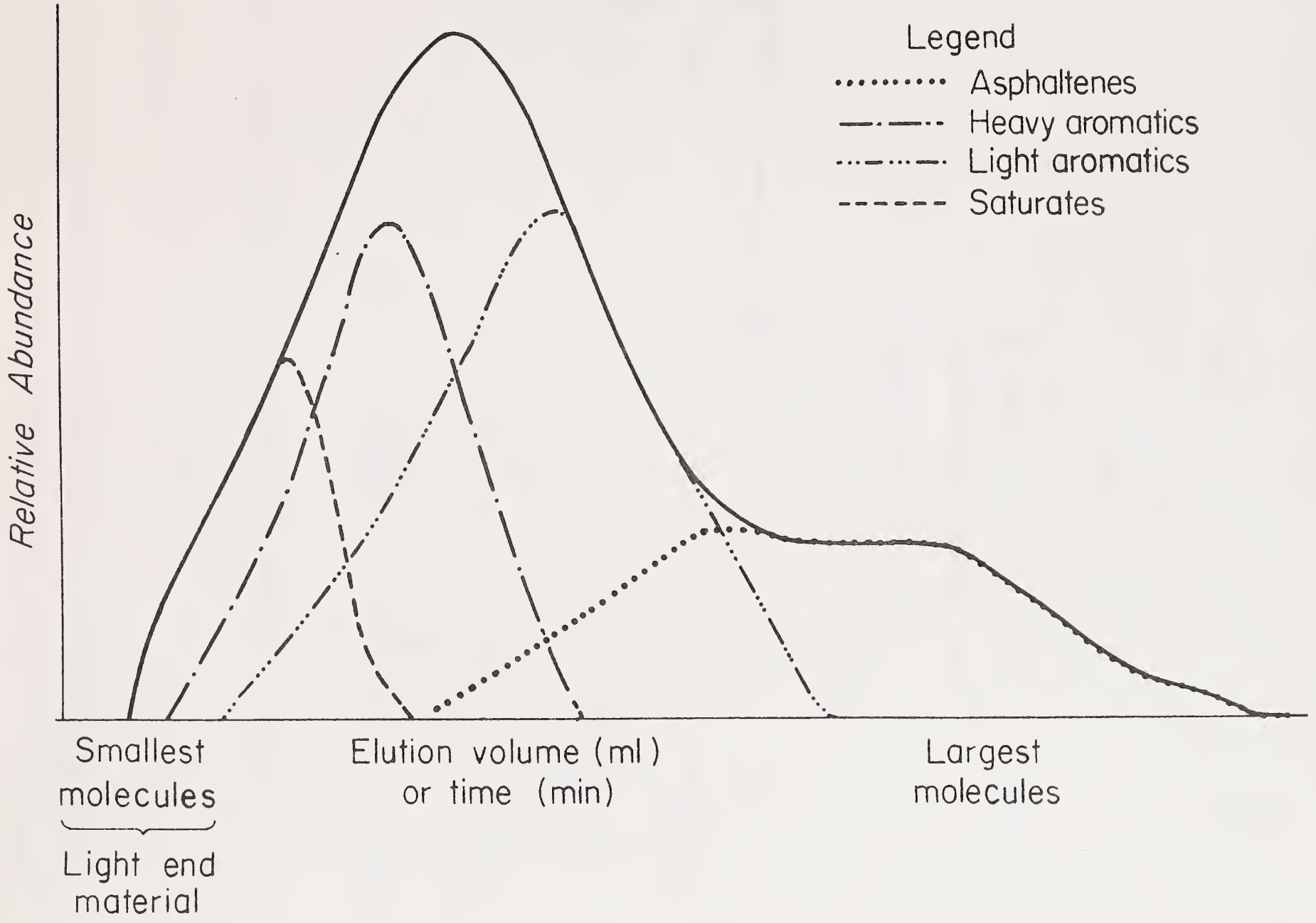
1. To determine if the method would show significant differences in molecular size distribution between the asphalt from good and bad roads.
2. If so, could these differences be related to the performance of a given road? It was anticipated that differences might correlate with cracking of pavement.
3. If so, could these differences be used to generate a high quality model of asphalt for comparison?
4. If a high quality model of asphalt from a good bituminous pavement could be obtained, then this model might be used to predict some characteristics of road performance.
5. Perhaps new asphalt specifications could be written based on this method.

Discussion of the HPLC method for measuring the molecular size profile of asphalt:

The high pressure part of HPLC is a new procedure which speeds up the analysis time and therefore makes this method applicable to asphalt analysis. In this method a complex mixture (asphalt) is forced at high pressure (2000-6000 psi) through a column of small beads which separates the mixture into various molecular sizes. When the material emerges from the outlet end of the column, the aforementioned mixture is now separated into fractions of equal molecular size. The larger molecules will come out first followed by smaller and smaller molecules until finally the light end material is expelled.

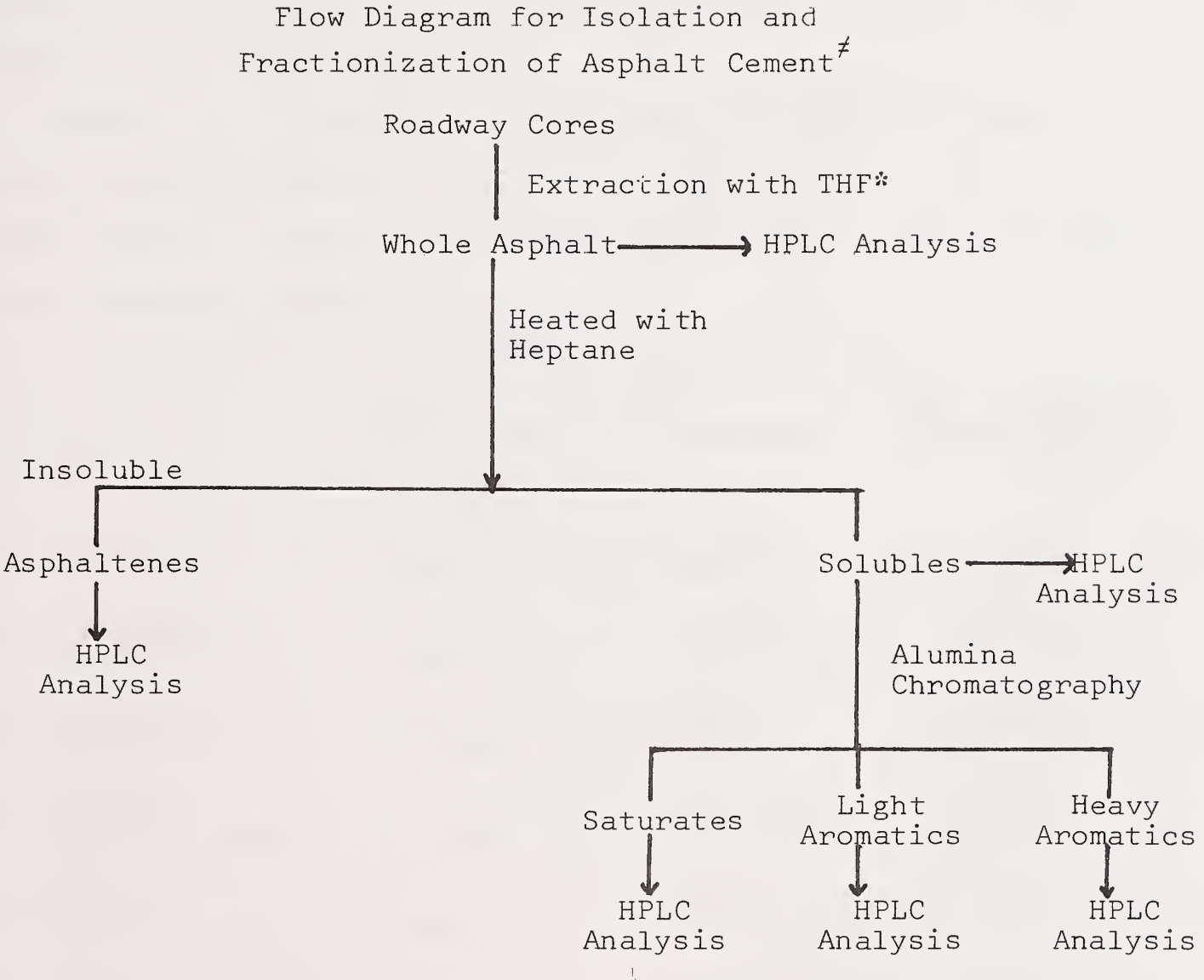
A refractive index detector is used to monitor the effluents and produces a graph of the results by means of a strip chart recorder. In Figure 1, a molecular size profile of an asphalt sample is shown containing some pertinent details. The molecular size profile is the solid line. As stated above, the largest molecules come through the column first which is the right edge of the graph. These are followed by a continuous series of smaller sized molecules until finally the light ends emerge (left side of graph). The height of the profile at any particular point shows the amount or relative abundance of that particular molecular size. The sectioned areas underneath the overall profile show the approximate sub-fractions of asphalt: asphaltenes, heavy aromatics, light aromatics and saturates.

FIGURE 1
MOLECULAR SIZE PROFILE
(Whole Asphalt)



Prior to discussion of the results of HPLC analysis, flow diagram 1 is presented to enhance the reader's understanding.

Flow Diagram 1



≠For detailed discussion of these procedures, see Experimental Section.

*Tetrahydrofuran

In the following sections, asphalt quality of various roadways is discussed. Diagrams and profiles such as those presented above will be used.

Analysis of asphalts from various sources using HPLC, Penetration and Ductility Tests.

A. Established Roads - 100/120 Penetration Design

With the help of Mr. T. Martin, Mr. R. Rask, and Division Laboratory Supervisors, six asphalt roadways were selected for sampling and complete analysis.

From a 1/4 mile section of each road, 10 cores (4" diameter) were abstracted from the outside tire lane. Table 1 shows the roads sampled, refineries from which the asphalt originated and some pertinent details.

Table 1

Project	Design Penetration	Refinery	Date of Project Completion
	100/120		
1. F 215(16) U1 Lolo-Missoula	100/120	Phillips	11/29/68
2. I 90-1(30)50 U1 Superior-East	100/120	Phillips	12/7/66
3. I 90-2(13)78 U1 Alberton-East	100/120	Exxon	12/8/63
4. F 157(19) Miles City-Jordan	100/120	Continental	6/5/64
5. F 217(11) Gardner-Livingston	100/120	Cenex	1965
6. I-IG 90-6(2)309 U1 Rocky Canyon Section	100/120	Cenex	1963

The procedure followed for extraction, fractionation and analysis is that described previously on pp.4-5. Figures 2-7 show a comparison of molecular size profiles between the Lolo-Missoula (Lolo) and the Miles City-Jordan (MC-J) projects. The three individuals mentioned above along with Dr. Spittler subjectively rated the Lolo project as good in quality and

MC-J as poor to bad in quality. Albeit this judgment was subjective, the prime criteria for determining a good roadway mat was when transverse, longitudinal, and alligator cracking was not prevalent.

These two projects will be discussed at length to acquaint the reader with the overall analysis. Only summaries of the other 4 roads will be given. A complete set of data for each road is provided in the appendix if the reader wishes to examine them more carefully.

From the molecular size profile shown in Figure 2, one can see that the whole asphalt of MC-J contains more asphaltenes than Lolo and it is of lower molecular size. Further, Lolo appears to have heavy aromatics of higher molecular size. However, most distinguishing in these two profiles is the fact that the light aromatics and saturates of MC-J contain material of much lower molecular size than Lolo.

The HPLC molecular size profiles of the sub-fractions will show in detail where these two asphalt samples differ. The asphaltene fraction profile shown in Figure 3 reveals an overall lower molecular size for MC-J. The soluble fraction* profile shown in Figure 4 shows more clearly that the light ends of MC-J are quite low in molecular size. The molecular size profiles of the sub-fractions contained within the soluble fraction are shown in Figures 5, 6, and 7.

---

* The soluble fraction means that portion of the crude asphalt which is soluble in heptane. It contains the sub-fractions, heavy aromatics, light aromatics, and saturates. See separation flow diagram, page 5.

FIGURE 2

HPLC ANALYSIS OF WHOLE ASPHALT

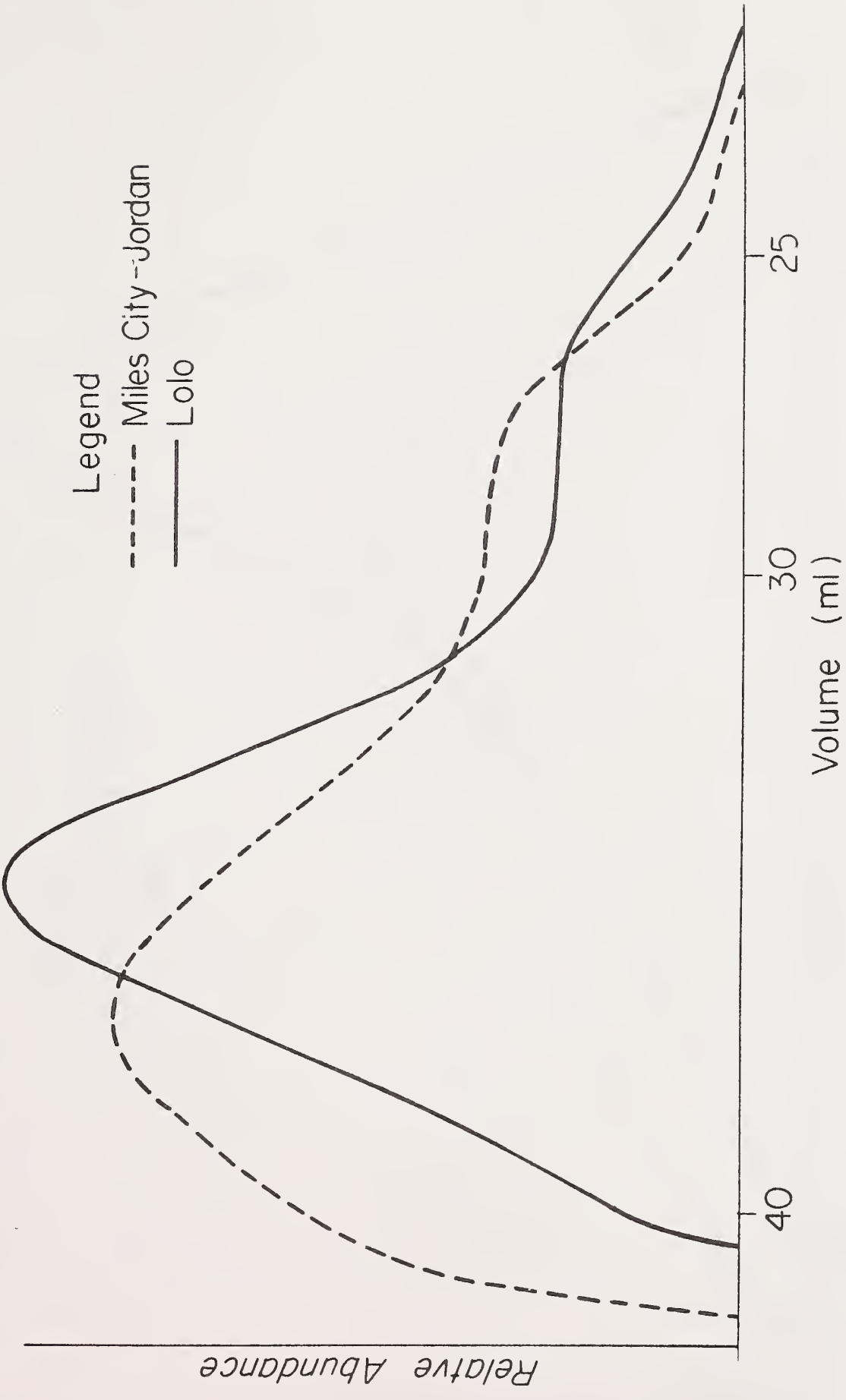


FIGURE 3

HPLC ANALYSIS OF ASPHALTENES

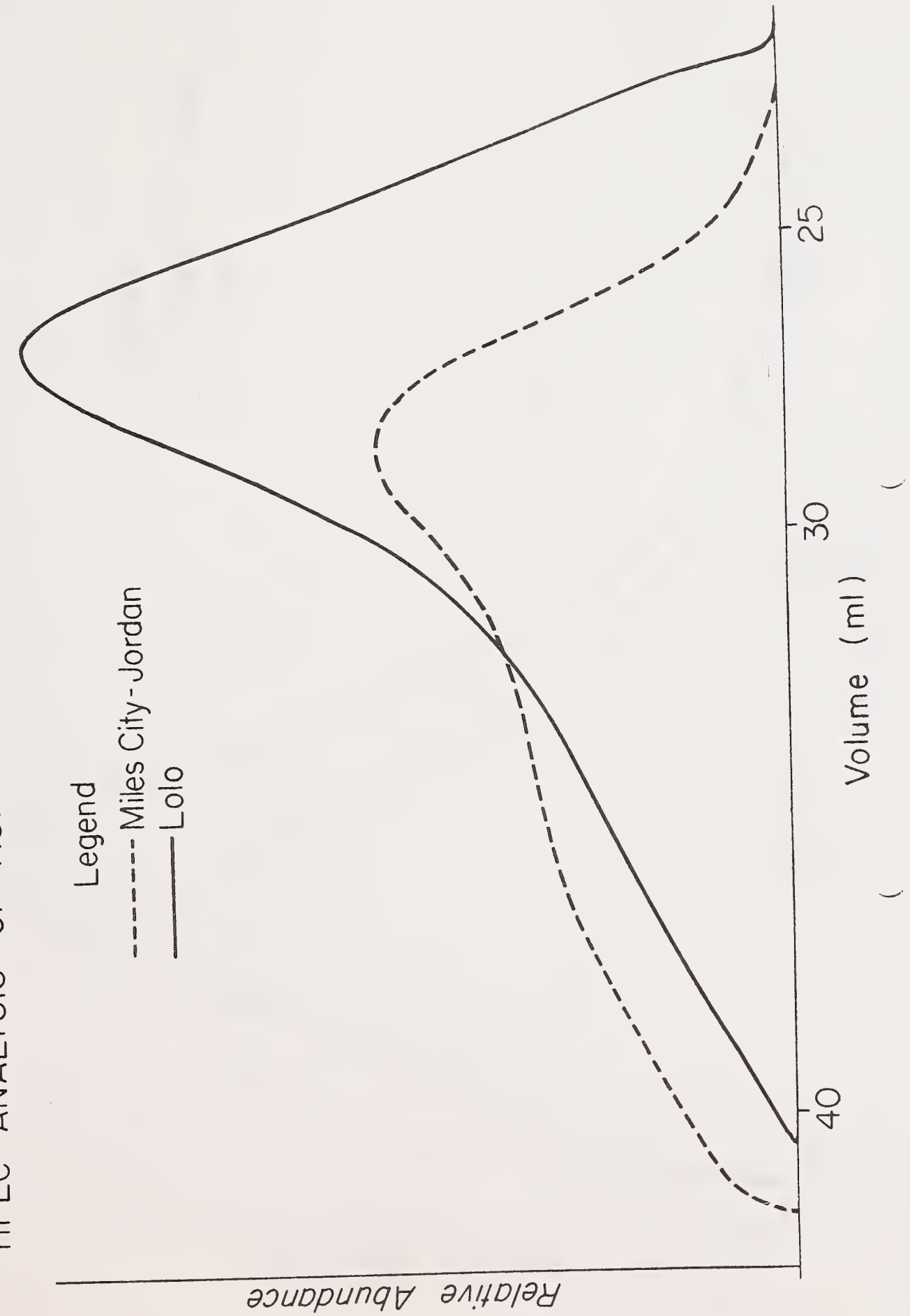


FIGURE 4

HPLC ANALYSIS OF SOLUBLE FRACTION

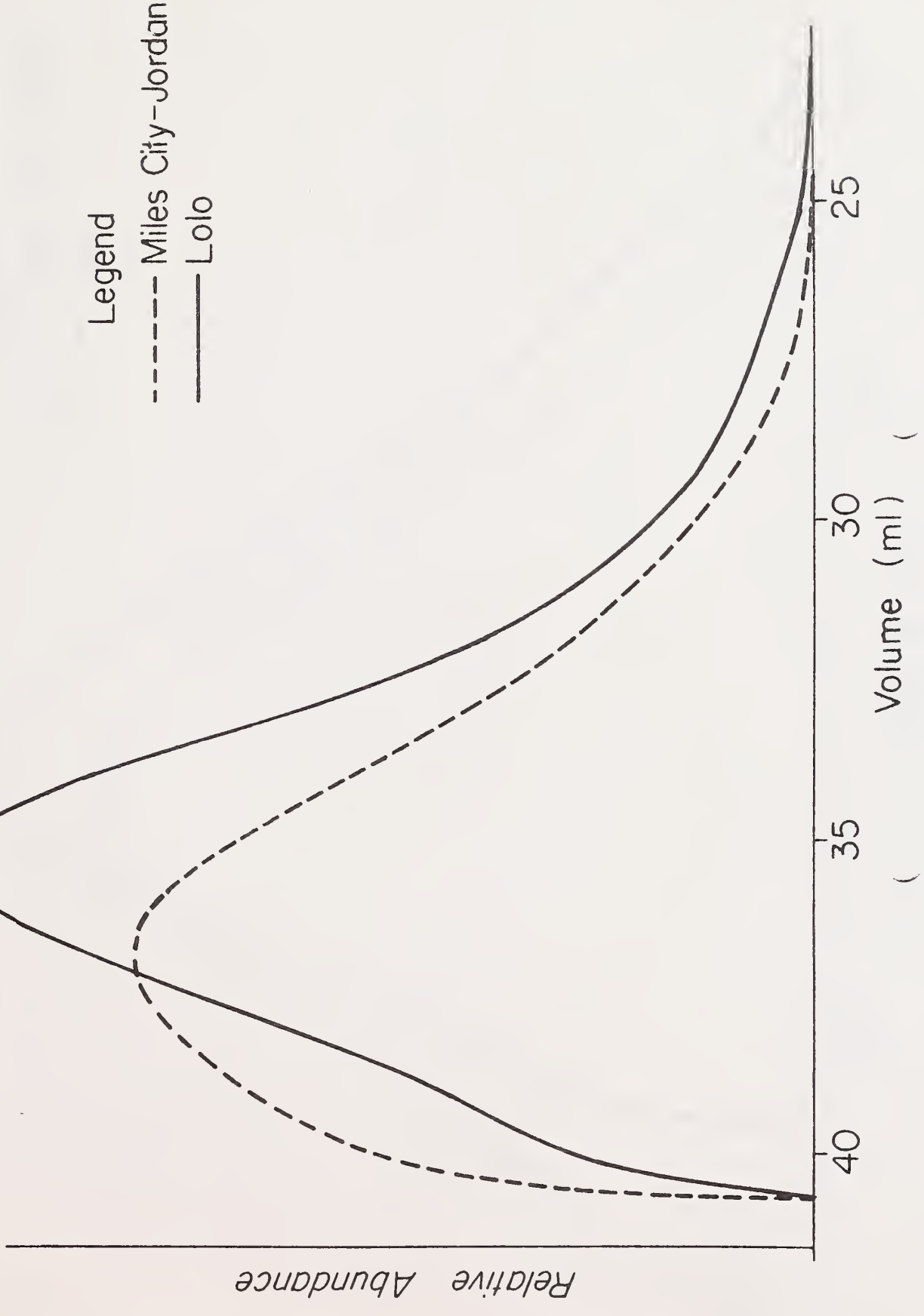


FIGURE 5

HPLC ANALYSIS OF HEAVY AROMATICS

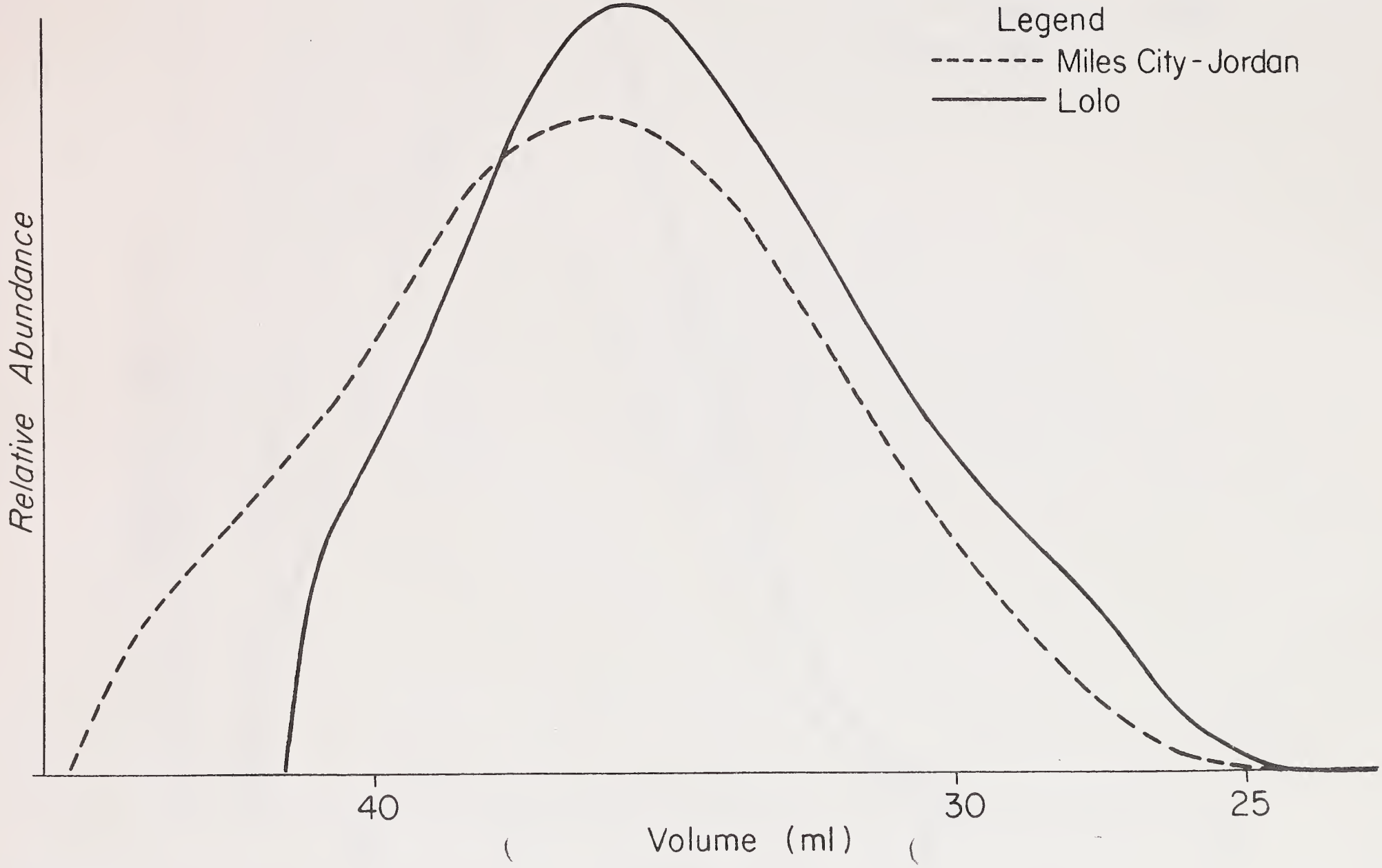


FIGURE 6

HPLC ANALYSIS OF LIGHT AROMATICS

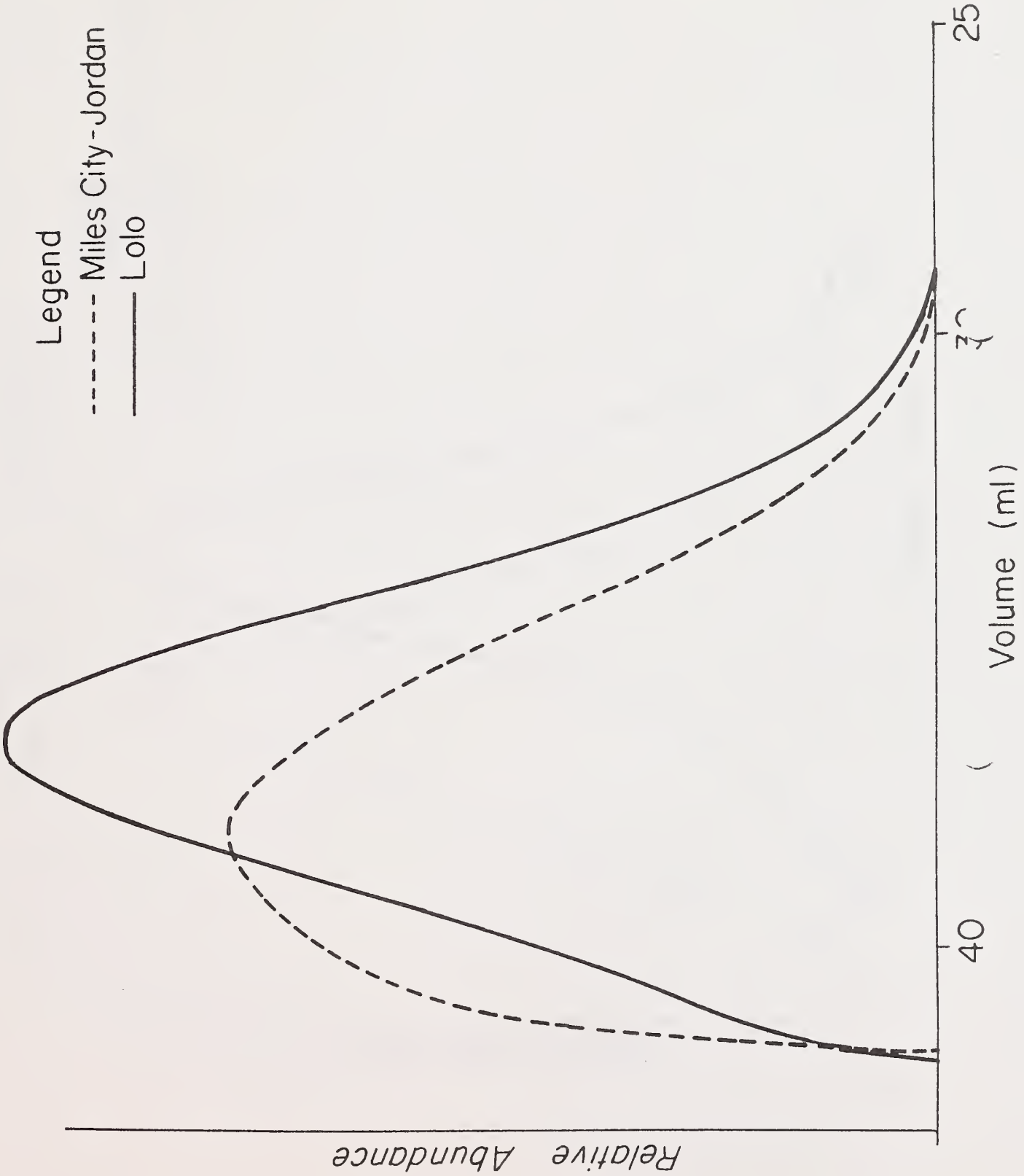
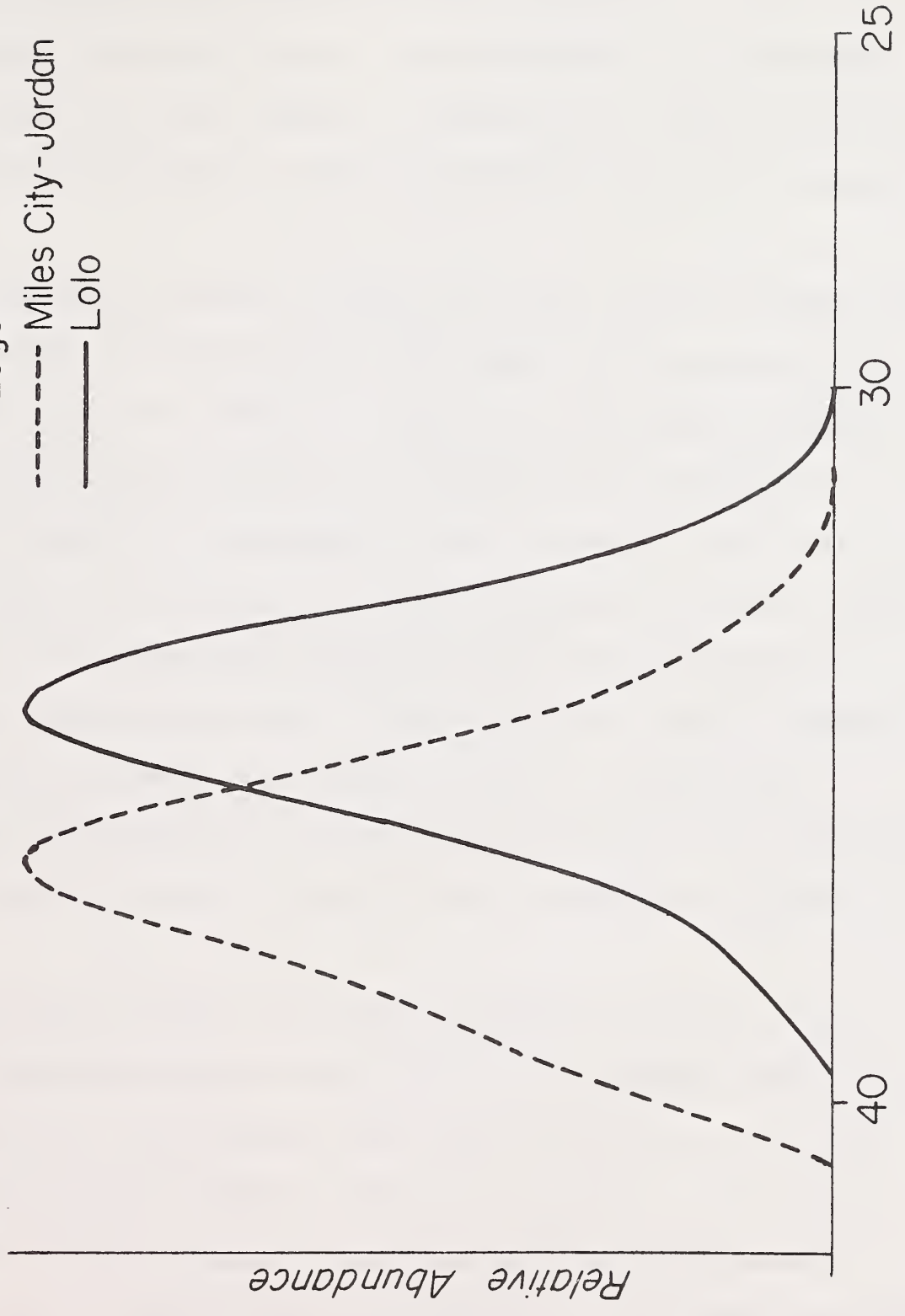


FIGURE 7
HPLC ANALYSIS OF SATURATES



Comparison of the heavy aromatic profiles reveals almost complete similarity at the high molecular size end. At the extreme left on the graph, lowest molecular sizes, the MC-J material is again smaller. In the light aromatic fraction, however, the peak or most abundant fraction is smaller sized for the MC-J asphalt. Finally, and as expected, the molecular size profile for the saturates of MC-J are of considerably lower molecular size.

The conclusion with regard to this road is that it (MC-J) contains far too much asphaltene causing hardening which cannot be counteracted by the smaller sized asphalt sub-fractions. Since this road exhibited cracking within the first year after completion, it appears that the amounts of asphaltenes to sub-fraction materials were not in balance. This means that either the original asphalt was out of specification or the original asphalt was softened by extremely light end material which evaporated quickly leaving a very hard material behind. This evaluation is further augmented by the following data presented in Tables 2 and 3. In these tables Alberton-East asphalt analyses are also presented because it has a molecular size profile which is similar to MC-J and also has extensive alligator cracking.

As can be seen in Table 2, both MC-J and Alberton asphalts contain much larger amounts of asphaltenes and are lower in saturates compared to Lolo. The amounts of light aromatics for these two roads are also lower than those of Lolo. The Alberton roadway is not cracked as extensively as MC-J. Data in Table 2 suggests that the asphalt from the Alberton project is closer in composition to Lolo than MC-J is. The lower asphaltene content and higher amounts of heavy and light aromatics in the Alberton asphalt may explain why it has fewer cracks than MC-J.

Physical measurements of these three asphalts, Table 3, completes the story. Lolo has retained a higher penetration over the 9 years of its existence than MC-J has in 13 years and Alberton in 14 years. It is not known exactly when cracking began on the Alberton road. The ductility measurements at 77°F. are not of much value, but those at 40°F. clearly distinguish these asphalts which correlates well with the extent of roadway cracking.

Table 2

Asphalt Fraction	Percent of Sub-Fractions Lolo	MC-J	Alberton-East
Asphaltenes	16.63	26.32	20.58
Heavy Aromatics	38.23	34.38	40.73
Light Aromatics	32.84	20.46	25.07
Saturates	14.50	9.68	9.43
% Recovery*	102.20	90.84	95.81

*If we recovered all the asphalt in the sub-fractions this number would be 100. Numbers above 100 reflect experimental error and incomplete solvent removal.

Table 3

Design Penetration 100/120

Project	Roadway Condition	Penetration at 77°F (avg. of 3 tins)	Ductility (1 cm/min.) 40°F	Ductility (5 cm/min.) 77°F
Lolo (11/29/68)≠	good	89±2	26	145+
MC-J (6/5/64)	poor	55±4	13	145+
Alberton-East (12/8/63)	poor	21±4	0⊕	137

⊕Due to experimental error, this # could be as high as 6 or 7.

≠Date of Project Completion.

Analysis of asphalts from the other roads in this penetration class using molecular size profiles, quantitative amounts of sub-fractions, and physical tests enabled us to classify these roads. Actually the quality of asphalt has been rated and found that it correlates to the relative extent of cracking.

	Project	Rating Quality	Remarks
		Rating	
1.	Lolo-Missoula	good	
2.	Rocky-Canyon	good	Actually should be rated excellent considering its age of 14 years.
3.	Superior-East	fair	
4.	Gardner-Livingston	fair	Project #F 217(11)
5.	Alberton-East	poor	It does not have enough light ends and low molecular size components to counterbalance the asphaltenes.
6.	Miles City-Jordan	bad	The only thing holding this road together is the light ends and lower molecular sizes.

A complete set of physical test data on the asphalts of these roads may be found in Table 6. Molecular size profiles are located in the appendix.

Since this discussion of asphalts from roads of 100/120 penetration design has been long and detailed, a summary is presented.

Visual observations revealed that the Lolo-Missoula road was good and Miles City-Jordan and Alberton East roads had cracked extensively. The asphalt and analyses thereof were used as the starting point or base for interpretation. Assuming Lolo to be a good road, the HPLC molecular size profiles and fraction quantities show MC-J and Alberton-East asphalts to have too much high molecular size material and too little of the small sized components to keep the roads from cracking. In addition, the MC-J asphalt contains low end material of very low molecular size. Penetration and ductility tests of these asphalts also clearly indicate the condition of these three roadways.

Complete analysis of all the asphalts has led us to classify the entire class of roads into good, fair, poor and bad.

B. Established Roads - 120/150 Penetration Design.

Only one sample of this grade was obtained and analyzed.

It was Project #I 94-3(23)105 U1, Rosebud-East, which was judged to be only of fair quality. Continental Refinery supplied the asphalt and the project was completed May 5, 1971. Discussion of this road in more detail will be reserved until the new roads section but it is important to remember that it is only a fair quality road.

C. Established Roads - 150/200 Penetration Design.

Two roads were analyzed in this class. They were:

	Quality	Refinery	Completed
I-IG 90-7(9)327 U1 Livingston S.& E. (Liv. S&E)	good	Exxon	1962
F 217(12) Gardner-Livingston Rd. (G.L.12)	good	Cenex	8/22/61

Mr. Martin and Mr. Rask think Liv. S&E is the best road of all those investigated. Since both roads are 15 and 16 years old and were judged good this year, they should be analyzed as primary standards of this class. Molecular size profiles of the whole asphalt for these two roads are compared in Figure 8.

I would tend to judge the asphalts of these two roads similar, but must qualify that statement slightly by saying the Gardner-Livingston road has the higher molecular size components. The physical data shown in Table 4, reveal that indeed this is so as the Gardner-Livingston (GL) asphalt is harder with a ductility equal to 6.6 when measured at 40°F.

Table 4

150/200 Penetration Design

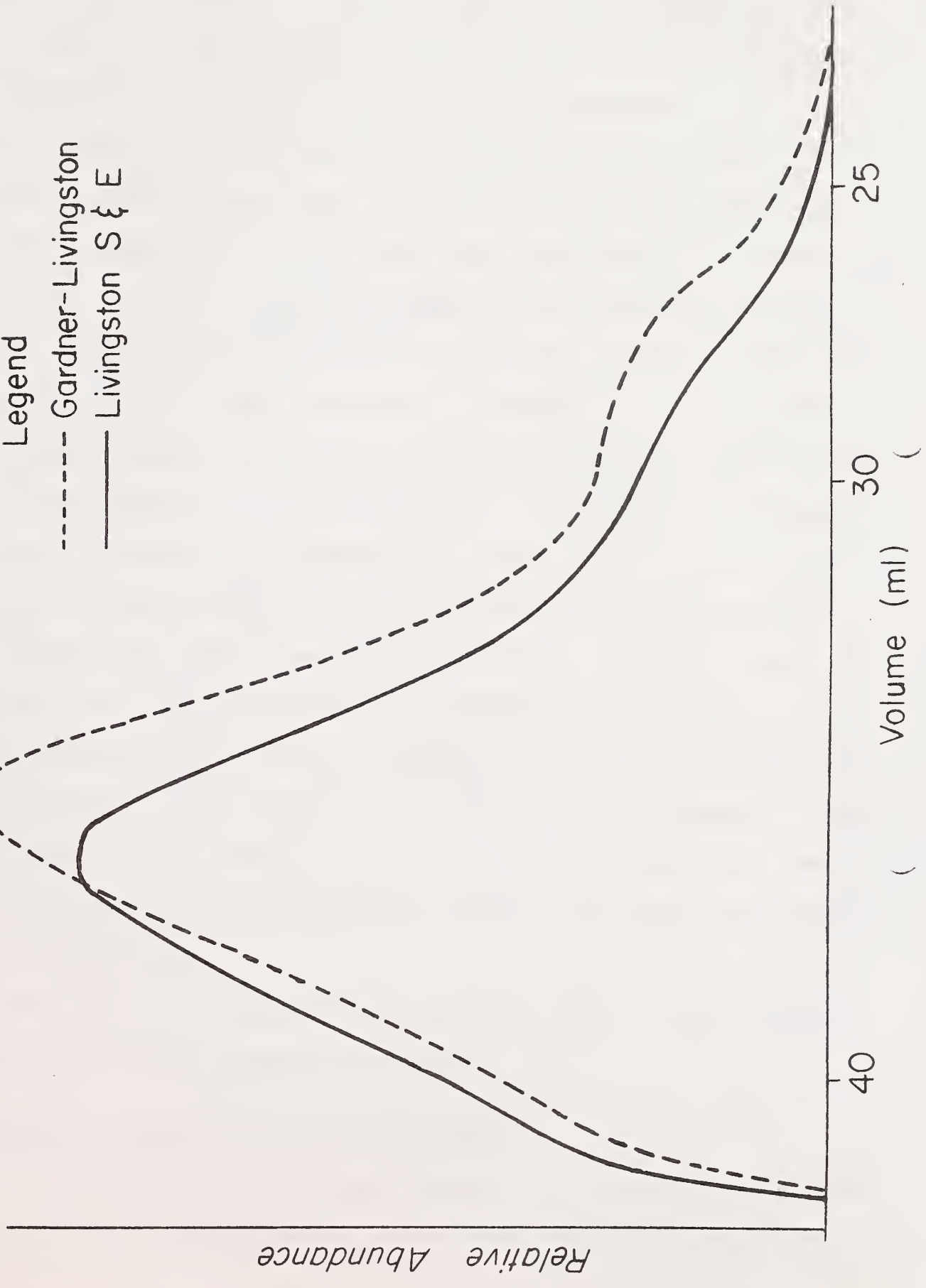
Project	Roadway Condition	Penetration at 77°F	Ductility 40°F	Ductility 77°F	Year Completed
I-IG 90-7(9)327 U1 Livingston S.&E.	good to excellent	81 ±3	29.5	141	1962
F 217(12) Gardner-Liv. Rd.	good	64±6	6.6	145+	1961

Percentages of Sub-fractions

	Gardner-Liv(12)	Liv. S.&E.
Asphaltenes	16.18	16.56
Heavy Aromatics	39.80	34.93
Light Aromatics	31.95	32.07
Saturates	11.31	10.59
% Recovery	99.24	94.15

FIGURE 8

MOLECULAR SIZE PROFILE OF WHOLE ASPHALT



The penetration values also reflect additional hardness in the Gardner-Livingston sample. Finally, excess amounts of the heavy aromatic fraction in GL asphalt may be what is really contributing to its hardness and ultimate cracking of the roadway.

The sub-fraction profiles give a better picture of the differences between these roads (Figures 9-12). The asphaltene fractions are quite equivalent, but the heavy aromatic fraction of the GL asphalt is, as predicted, higher in molecular size than Liv. S.&E. This would contribute to its extra hardness. The differences between the light aromatics of these two asphalts are insignificant. Comparison of the saturates which contribute positively to the softness of the asphalt are significantly different. Gardner-Livingston(12) has higher molecular size material, less soft, than Livingston S.&E. Both of the saturate fractions are of high enough size that they won't evaporate. In conclusion, it appears that the subtle difference between these roads is in the heavy aromatics and saturates. The only reason the Liv. S&E road is not cracking yet is that it has a slightly lower molecular size which lends to its flexibility while GL has a bit too much heavy aromatic fraction of high molecular size and its saturates are too high in molecular size.

In conclusion, Livingston S&E should be used as the standard of comparison for this penetration grade.

D. New Road - 120/150 Penetration Design

In the previous sections where asphalt analyses were discussed, prior knowledge of the pavement quality was known. In this section,

FIGURE 9
HPLC MOLECULAR SIZE PROFILE OF ASPHALTENES

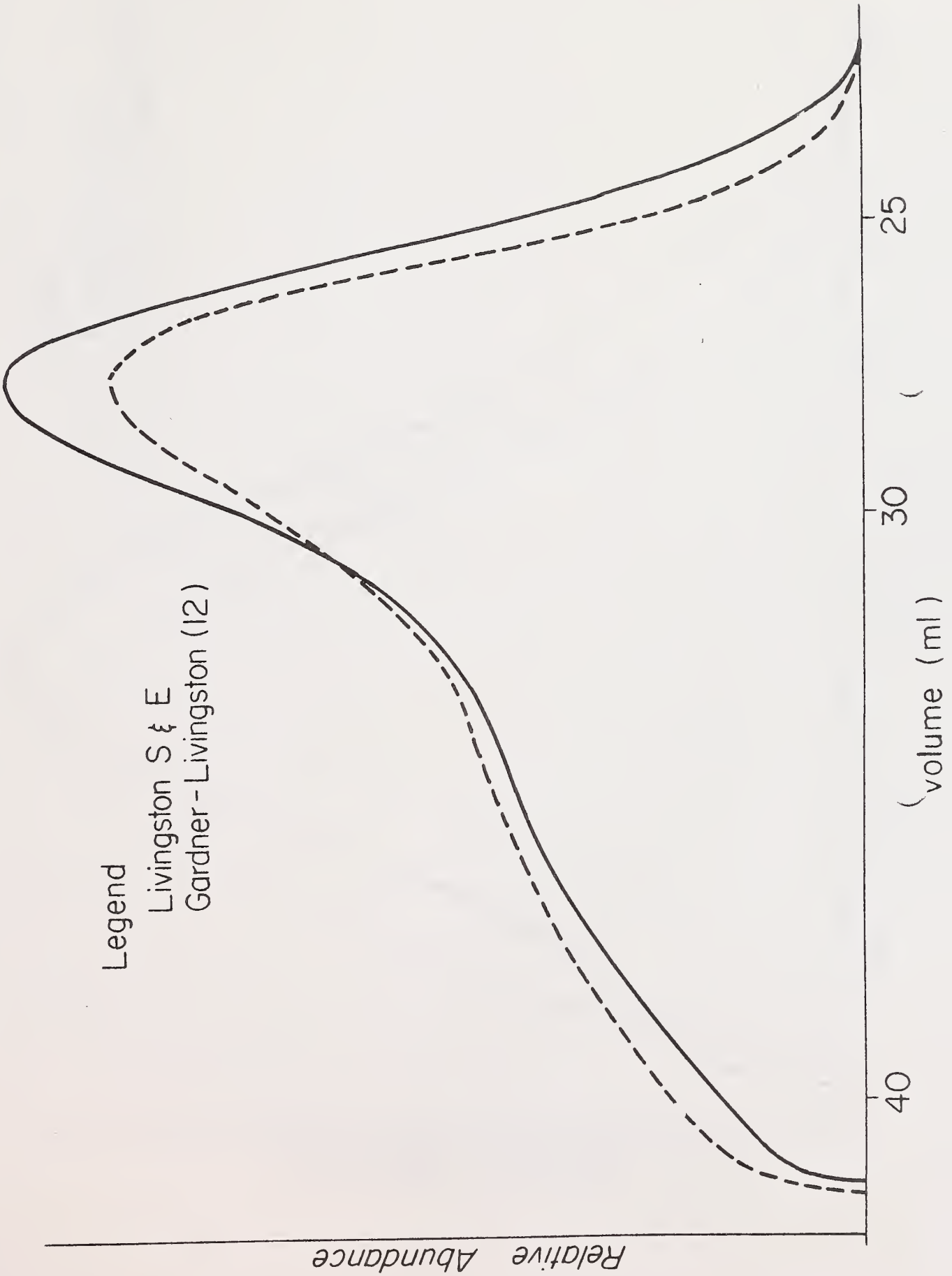


FIGURE 10

HPLC MOLECULAR SIZE PROFILE OF HEAVY AROMATICS

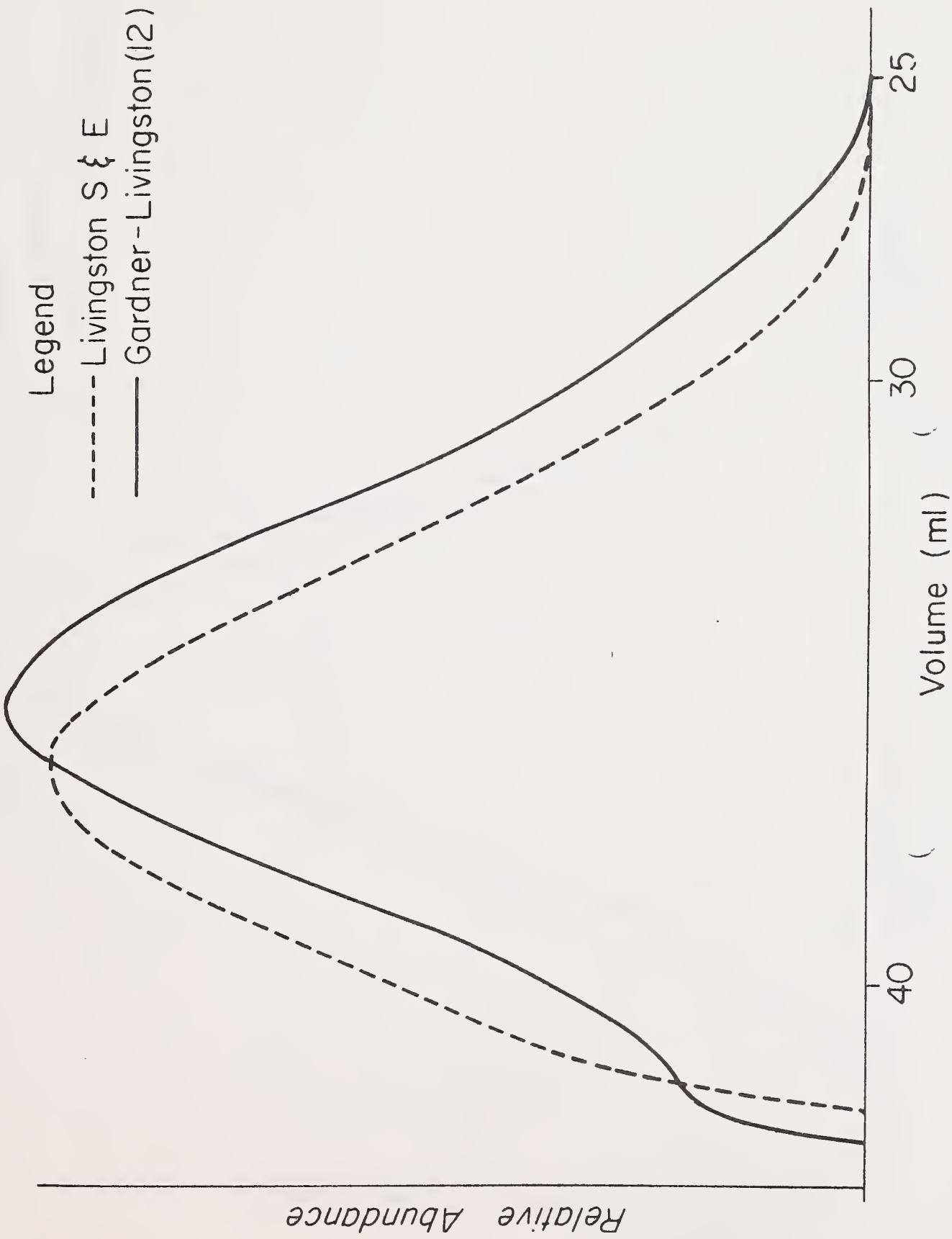


FIGURE 11

HPLC MOLECULAR SIZE PROFILE OF LIGHT AROMATICS

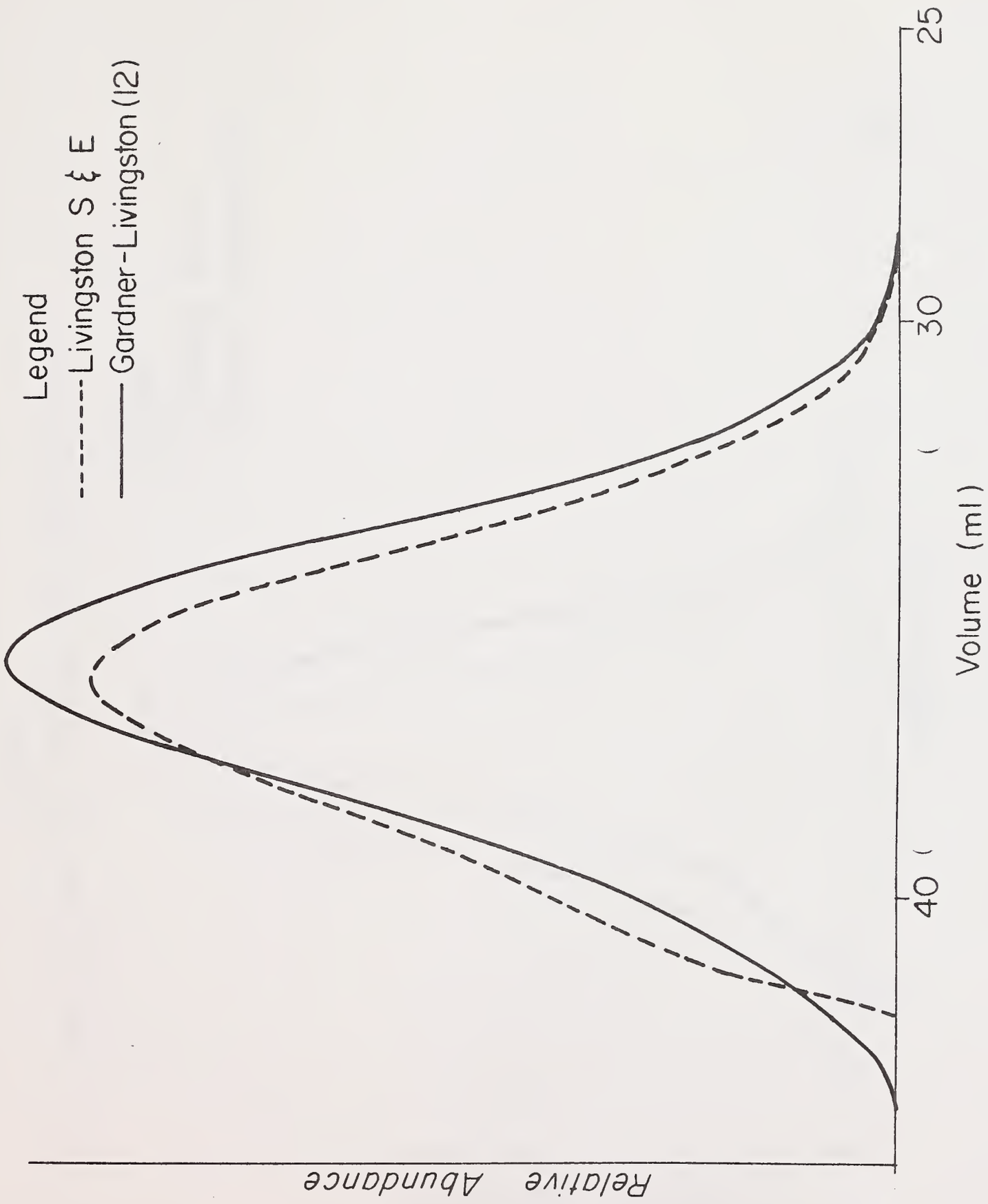
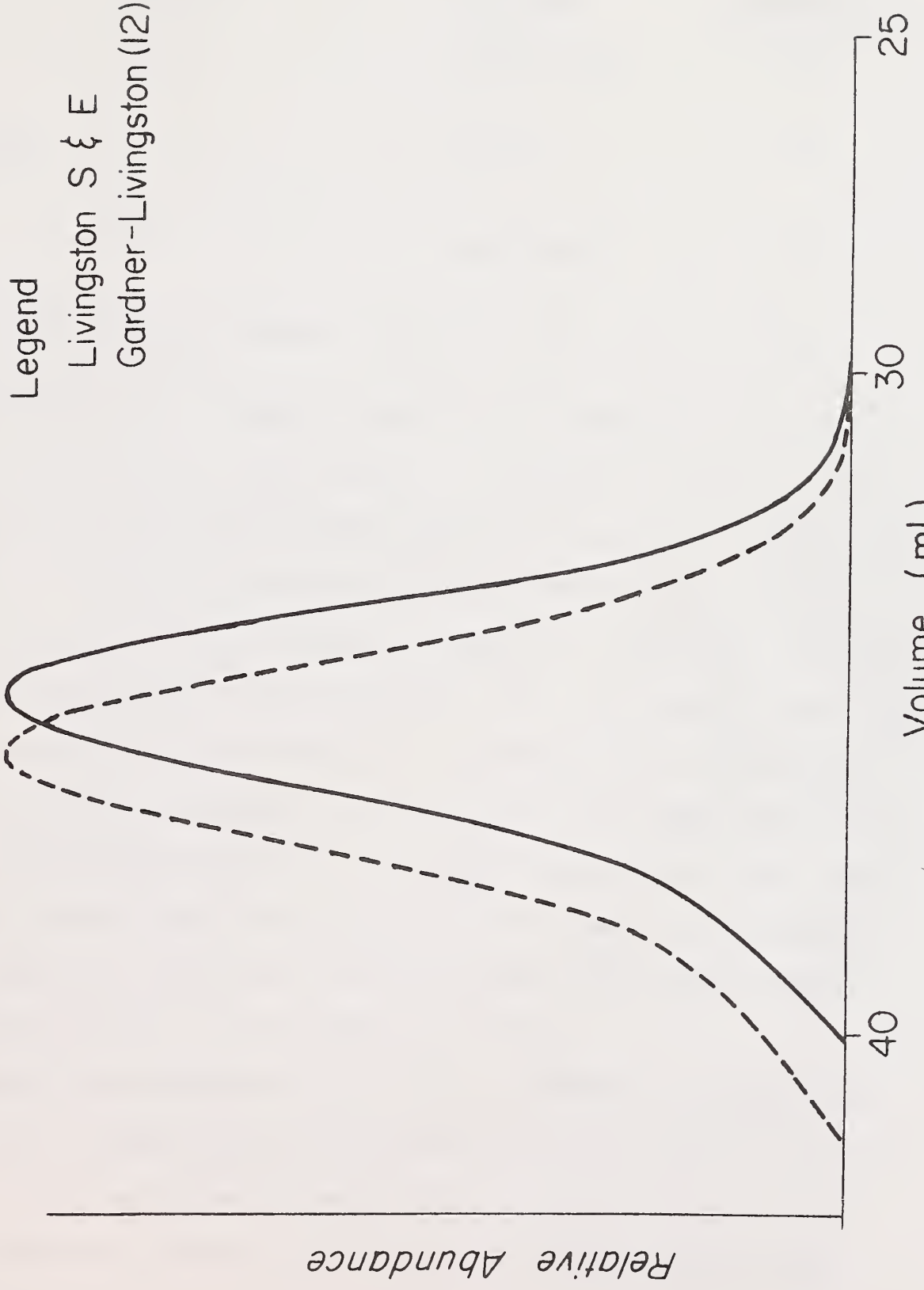


FIGURE 12

HPLC MOLECULAR SIZE PROFILE OF SATURATES



the asphalts from two new roads are discussed and compared to asphalt from one roadway of only fair quality. These three pavement projects are:

Project	Quality	Refinery	Completion
I 94-3(23)205 U1 Rosebud-East	fair	Continental	1971
I 90-7(36)321 U1 Bozeman Pass East Transport**	?	Cenex	1977
F 64-1(1)0 Big Sky	?	Continental	1977

** Another layer of asphalt pavement will be laid on top of this material in 3 to 5 years.

A comparative set of whole asphalt molecular size profiles are displayed for these three roads in Figure 13. There is not much difference between the Bozeman Pass-East and Big Sky asphalts. However, the asphaltene content of both of these roads is not only lower in quantity, but lower in molecular size when compared to the profile of Rosebud-East asphalt. The sub-fraction profiles of all three are virtually identical except for the asphaltene fractions which are displayed in Figure 14. With some difficulty due to the differing heights of the graph, one can see that the peak for the Rosebud-East profile is to the right of the other two. This means the molecular size is higher for Rosebud-East asphalt, supporting the interpretation of Figure 13.

The physical and chemical data shown in Table 5 corroborate the conclusions reached from interpretation of the profile curves. For example, the ductility of Rosebud-East asphalt is very low and would indicate cracking has commenced. It has not been proved

FIGURE 13

HPLC MOLECULAR SIZE PROFILES OF WHOLE ASPHALT

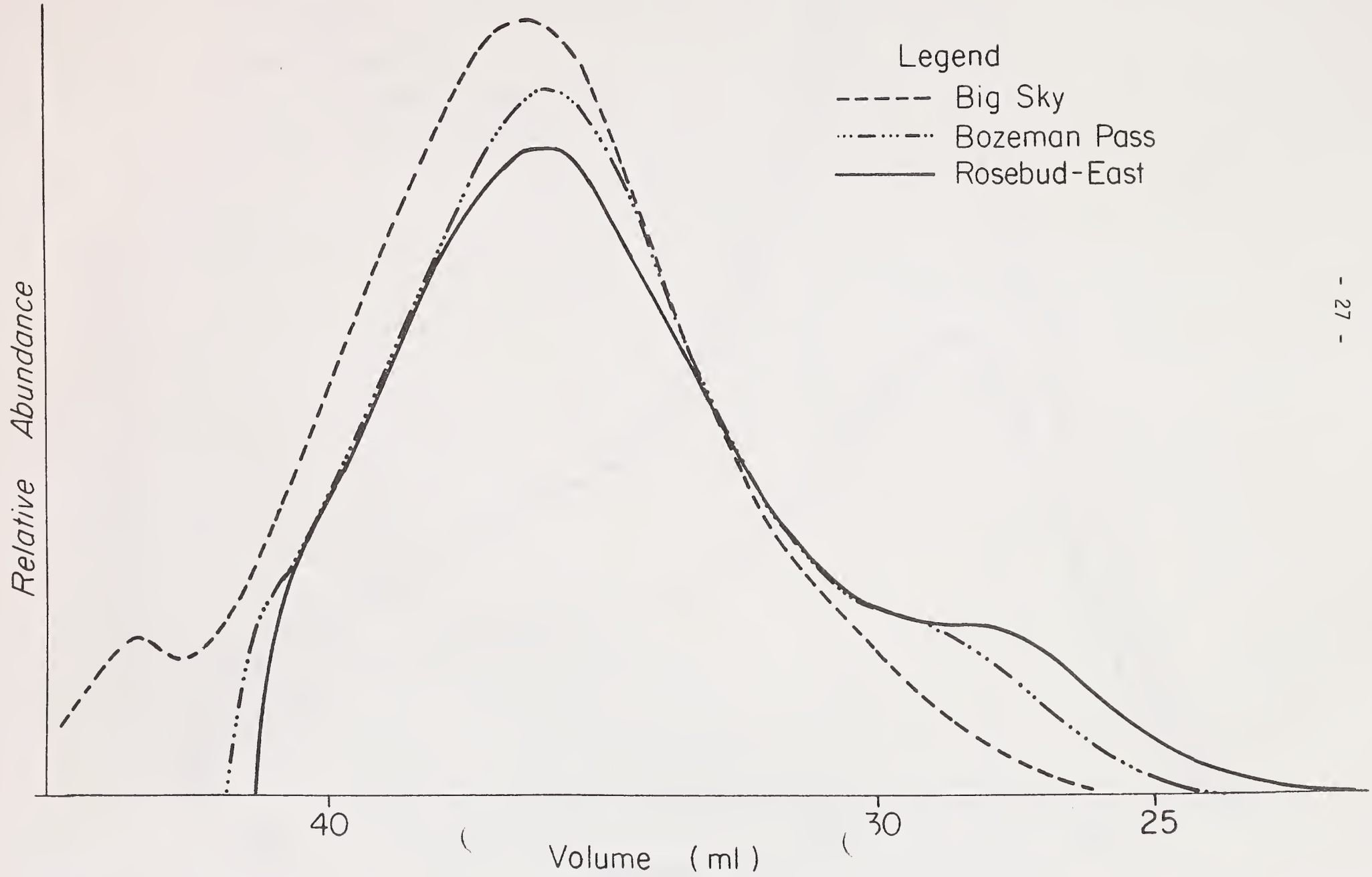
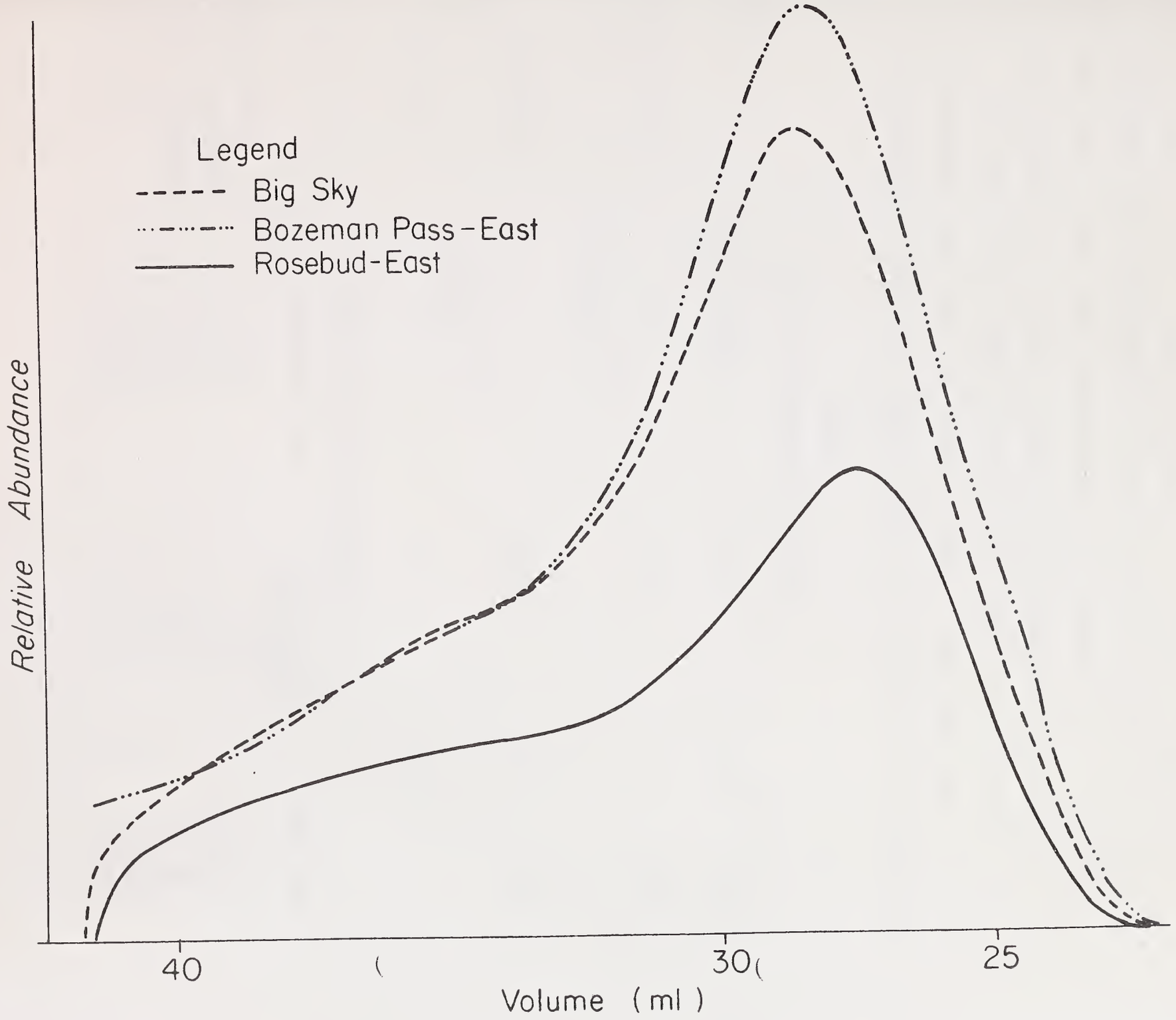


FIGURE 14

HPLC MOLECULAR SIZE PROFILES OF ASPHALTENES



that ductility data on asphalt from new roads are as useful as on aged roads. From the amounts of material in the sub-fractions, the asphaltene of the new roads appears too low. The other values for sub-fractions are satisfactory. Finally, the saturates of the new roads will not evaporate too fast.

In conclusion, these two new roads will be softer than Rosebud-East and will not crack so soon. However, they may be too soft. They are rated as fair in quality as a prediction.

Table 5

120/150 Penetration Design

Project	Quality (my judgment from data)	Penetration 77°F	Ductility 40°F	Ductility 77°F
Rosebud-East	fair	$96^{+}_{-}7$	4	145^{+}
Bozeman Pass	better than Rosebud			
Storage		$113^{+}_{+}1$	67	131
Transport		$113^{+}_{+}2$	85	106
Big Sky	better than Rosebud			
Hot Mix		112	68	

Percentages of Fractions

	Rosebud-East	Bozeman Pass (Storage)	Big Sky
Asphaltenes	14.08	11.74	11.02
Heavy Aromatics	33.32	36.51	34.77
Light Aromatics	34.73	38.92	35.45
Saturates	14.15	13.85	15.09
% Recovery	96.28	101.02	96.33

E. Effects of the Hot Mixing Process on Asphalt.

Both Bob Rask and I have felt there are two places where asphalt can be seriously deteriorated by heat. One is in the refinery processing, and the second is in the process where aggregate and asphalt cement are mixed at elevated temperatures. Figure 15 contains the profiles of whole asphalt from Bozeman Pass-East. One was from the storage tank and the other from the hot mix. As can be seen, there are virtually no differences between the two profiles. At least in this one instance, it must be concluded that the asphalt molecular sizes were not altered when mixed with aggregate under the conditions employed which were approximately 300° F in a Batch plant. A similar analysis was conducted on the Big Sky project. At this project, a Boeing Drum Dryer was used at a temperature of 245° F. The HPLC profiles are shown in Figure 16. In this example, the molecular size of the asphalt did change. The result is the formation of higher molecular sized asphaltene components. There are at least two explanations for this data. First, the asphalt supplied to the Big Sky project may be more susceptible to polymerization than the material used at the Bozeman Pass project. Second, there may be a zone in the Boeing Drum Dryer process which is very hot compared to the Batch plant process. Hydrated lime was used in both of these jobs and may be an important factor. Obviously, these findings need more research to reach a more definitive answer.

FIGURE 15

HPLC MOLECULAR SIZE OF WHOLE ASPHALT FROM BOZEMEN PASS-EAST

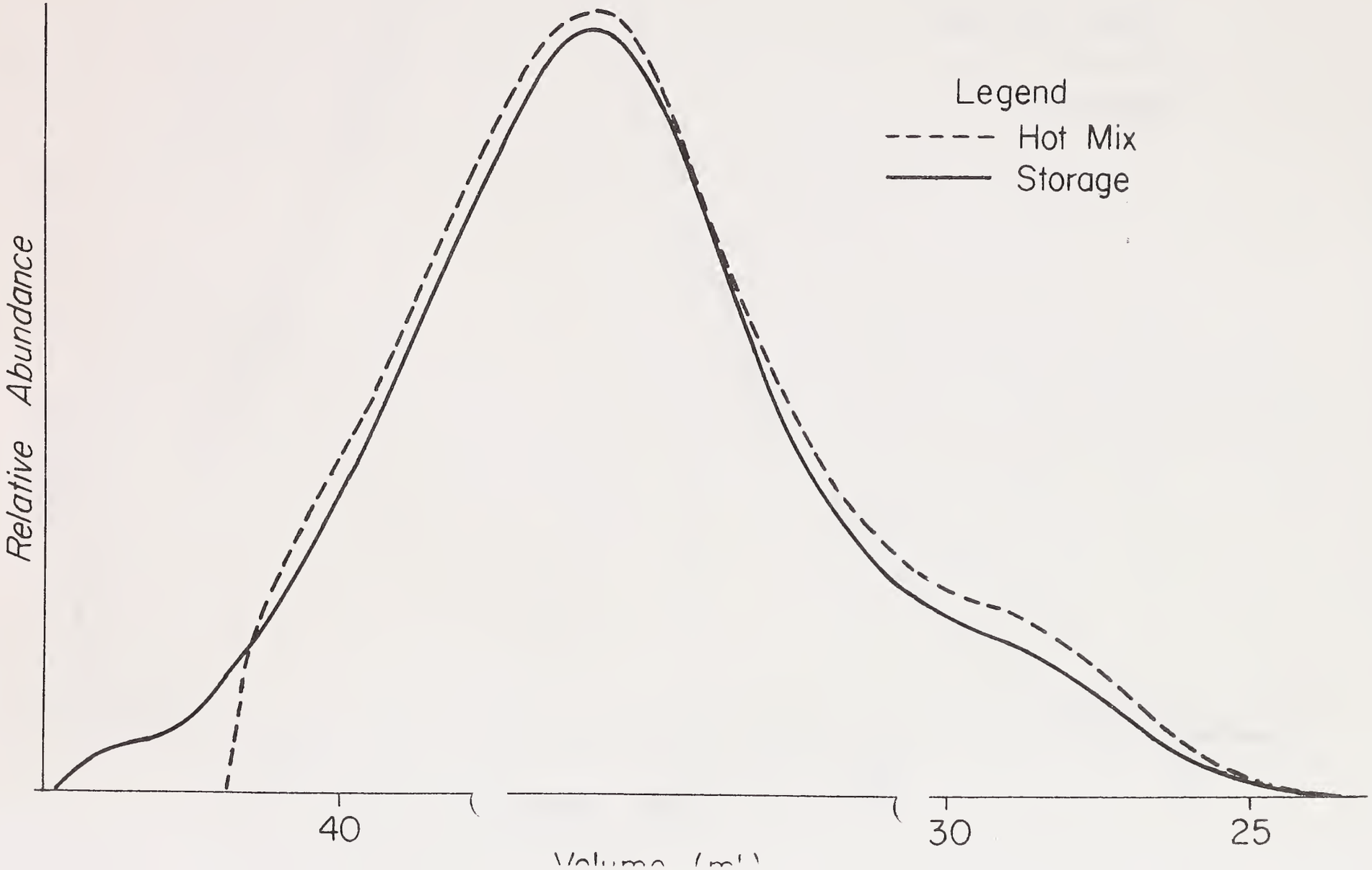
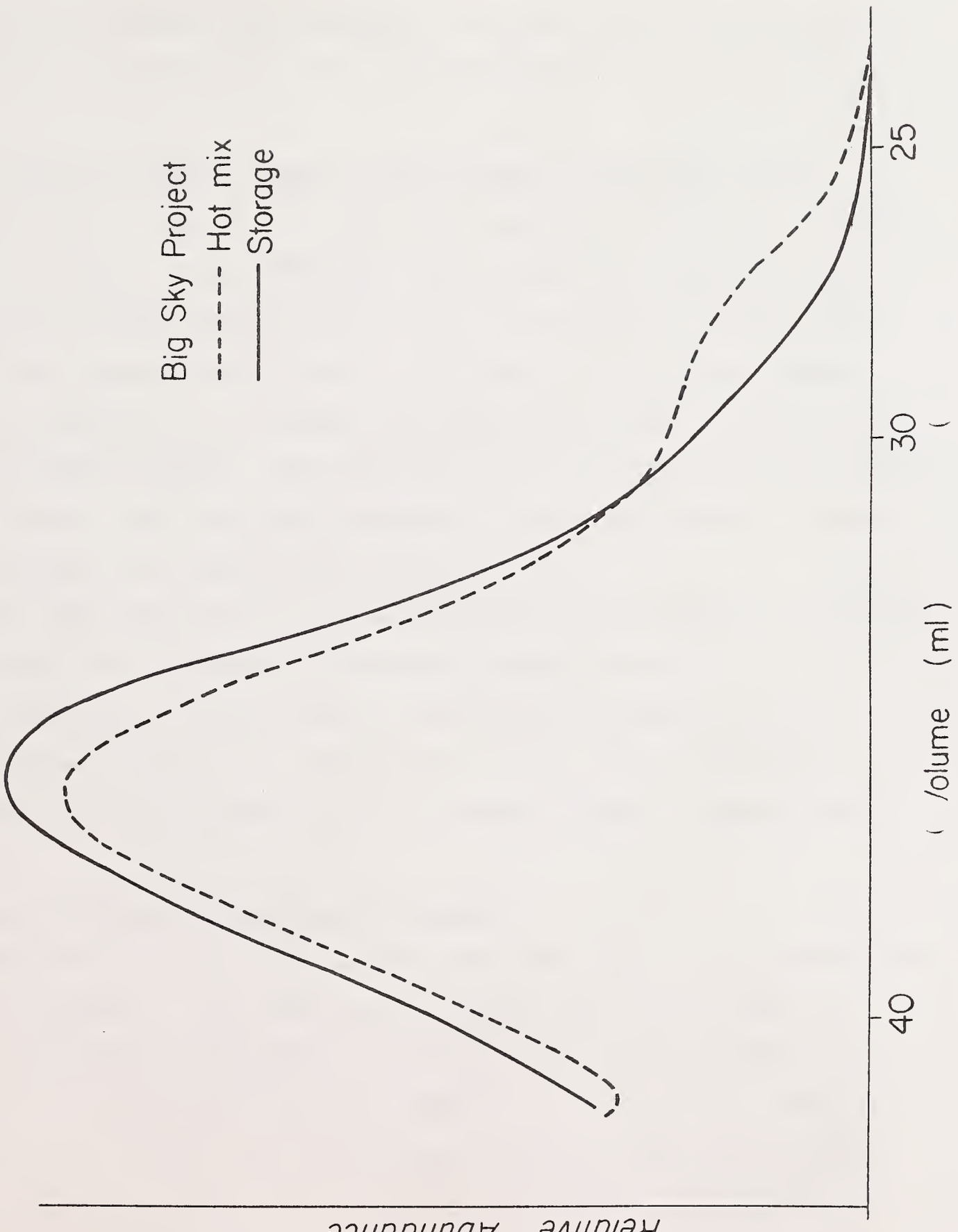


FIGURE 16

HPLC MOLECULAR SIZE PROFILE OF WHOLE PROJECT



Experimental Section

The flow diagram for isolation, fractionation, and HPLC analysis was given earlier on p. 5. The procedural details are given in this section.

1. Isolation of Asphalt Cement from Bituminous Pavement Cores.

The top 1/2 inch of each core was removed to avoid contamination from the surface. Then, three of these cores from a specific road section were placed in a 4-3/4" by 11-1/2" extraction thimble which, in turn, was placed into a Soxhlet extractor. The asphalt sample was then extracted with UV grade tetrahydrofuran (THF) until no more color was being removed. The time for this procedure involved between 1 and 3 weeks. THF was used instead of benzene or trichloroethylene because asphalt is more soluble in it.

After the extraction was completed, the solvent (THF) was removed via a Buchi roto-evaporator at reduced pressure and at 50° C. To remove additional traces of solvent the asphalt from the roto-evaporator was placed in a vacuum oven at 80° C for eight hours. This procedure was repeated until a constant weight of asphalt was obtained.

2. Fractionation of the Isolated Asphalt.

One gram of asphalt was removed from the isolate for fractionation and HPLC analysis. The remainder was poured into small tins and sent to the Montana Department of Highways for physical testing.

For fractionation, 1 gram of asphalt was refluxed with 100 ml of heptane for 3 hrs, and then filtered through a GFA glass filter using a millipore unit. The insoluble material plus the filter was again heated to boiling in 50 ml of new heptane and filtered. The solid remaining constituted the asphaltene sub-fraction. It was

dried in the vacuum oven to constant weight and then submitted for HPLC analysis.

The heptane filtrates were combined and evaporated to yield the solubles sub-fraction by rotc-evaporation. This material was dried, weighed, and submitted for HPLC analysis. About 80% of the solubles fraction was weighed and fractionated into saturates, light and heavy aromatics.

For this fractionation, the solubles were dissolved in 10 ml of heptane and pumped onto an activated alumina* column (15 mm x 250 mm). An FMI laboratory pump operating at ≈ 20 psi was used to put the solubles on the column. At this pressure, a flow rate of 1.94 ml/min was obtained.

After charging the column with solubles, 40 ml of heptane pumped through the column, bringing the saturate fraction off. When the solvent was removed, a colorless, semi-solid material resulted, which was dried, weighed, and analyzed by HPLC.

Fifty-five ml of benzene then pumped through the column, eluting the light aromatic fraction which was treated like the others. Finally, 25 ml of a mixture of MeOH-benzene (1:1) pumped through the column. This was followed by 20 ml of THF (1% H_2O) to remove the entire heavy aromatic fraction, which was treated as the others mentioned above.

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*The Baker reagent grade alumina was activated by heating in an oven at 450° for 8 - 10 hours.

3. HPLC Analysis of the Asphalt and Fractions Thereof.

Twenty-five mg of a sample dissolved in 25 ml of THF. One ml of this solution was then injected into the HPLC instrument to obtain the molecular profile. The eluting solvent was also THF and the pumping rate was 3 ml/min which corresponds to a pressure of 2000 psi. Four μ styragel columns (7.8mm ID x 30 cm) attached in series were used for the separation.

4. Materials.

a. Baker reagent grade Alumina and Altex Preparative Column Tubes were used for the alumina work.

b. FMI Laboratory Pump from Fluid Metering Inc., for low pressure separation.

c. HPLC from Waters Associates, included:

4 - μ Styragel Columns (3-500 Å and 1-1000 Å)

1 - M 6000 A high pressure pump

1 - Injection assembly

1 - Model R 401 differential refractometer for detection.

d. Solvents used were ultra pure grade distilled in glass from Burdick and Jackson.

e. Soltec Strip Chart Recorder.

Conclusions

1. The quality of asphalt in a bituminous roadway can significantly influence its performance.

2. A good correlation exists between asphalt quality and alligator or transverse cracking.

3. The chemical composition as determined by the HPLC method can be used to distinguish the differences between asphalts from good and bad roads.

4. The HPLC method provides a more detailed picture of the molecular size distribution in asphalt cements than any other method presently in use.

5. Quantitative determination of asphalt fractions, such as asphaltenes, light and heavy aromatics, and saturates, will augment the HPLC analysis and interpretation of asphalt quality.

6. Ductility measurements made at 40° F are more useful than those measured at 77° F, and should be performed on the residue after thin-film heating test.

7. A combination of HPLC analysis, fraction quantities (#5), and physical tests can probably be used to predict cracking of established roadways.

8. The HPLC method should be used to augment the present specification requirements of asphalt quality.

Implementation

Data gathered during the tenure of this grant showed that the HPLC method can show significant differences between various qualities of asphalt.

Therefore, recommendations to the Montana Department of Highways are:

1. Either purchase or acquire access to the equipment for HPLC analysis of asphalts.
2. Use this method to establish which roads in the state are the best in each penetration class. If a certain penetration design is going to be used for a project, the Highway Department should have, in hand, a model of the asphalt quality needed.
3. Use the method in concert with refineries to develop the best quality of asphalt.
4. Start running ductility tests at 40° F on the residue after thin-film heating test.
5. Use the HPLC method in concert with ductility at 40° F and penetration to predict when roadway cracking is likely to occur. Perhaps early treatment of a failing roadway may extend its performance.

REFERENCES

1. For an excellent review of asphalt specifications and performance measurements see: Anderson, D. I., Peterson, D. E., and Wiley, M., Characteristics of Asphalts as Related to the Performance of Flexible Pavements, Utah Project HPR State Study No. 925B, Utah Department of Transportation (June 1976).

2. Rostler, F. S., Rostler, K. S., Halstead, W. J. and Oglio, E. R., Fingerprinting of Highway Asphalts, Proceedings of the Association of Asphalt Paving Technologists, Vol. 41 (1972).

3. Lamb, Charles W., The Effect of Chemical Composition on the Rheological Properties of Asphalts, U. of Arkansas and Arkansas State Highway Department (February, 1967).

4. White, R. M., Mitten, W. R. and Skog, J. B., Fractional Components of Asphalt-Compatibility and Interchangeability of Fractions Produced From Different Asphalts, Proceedings of the Association of Asphalt Paving Technologists, Vol. 39 (Feb. 1970).

Physical Tests of All Roads Investigated

Project	Quality†	Penetration Original (1977)	Ductility 40°F	Ductility 77°F	Percentages of Fractions ASP	HA	LA	SAT	Completion Date
F 215(16) Ul Lolo-Missoula	good	100/120 (88)	26	145+	16.6	38.2	32.8	14.5	11/29/68
I-IG 90-6(2)309 Ul Rocky Canyon Section	good	100/120 (72)	29.5	145+	15.3	35.9	31.5	10.88	1963
I 90-1(30)50 Ul Superior-East	fair	100/120 (57)	9	145+	19.4	33.1	33.7	13.1	12/7/66
F 217(11) Gardner-Livingston	fair	100/120 (65)	9.5	145+	11.4	40.2	28.3	12.68	1965
I 90-2(13)78 Ul Alberton-East	bad	100/120 (21)	0	137	20.6	40.7	25.0	9.4	12/8/63
F 157(19) Miles City-Jordan	poor bad	100/120 (55)	13	145+	26.3	34.4	20.5	9.7	6/5/64
I 90-7(36)321 Ul Bozeman Pass-East (New road)	fair	120/150(113)	67	131	11.7	36.5	38.9	13.9	1977*
F 64-1(1)0 Big Sky (New road)	fair	120/150(112)	68		11.0	34.8	35.5	15.1	1977
I 94-3(23)105 Ul Rosebud-East	fair	120/150 (96)	4	145+	14.1	33.3	34.7	14.2	5/5/71
I-IG 90-7(9)327 Ul Livingston-S&E	good	150/200 (82)	29.5	141	16.6	34.9	32.1	10.6	1962
F 217(12) Gardner-Livingston	fair	150/200 (67)	6.6	145+	16.2	39.8	31.9	11.3	8/22/61

†Quality established by data from this project.

*An overlay will be put on in about 5 years.

APPENDIX

Discussion of HPLC Profiles Included in Appendix

The following graphs are the raw chromatograms of the various asphalt cements. They are organized in a manner consistent with main text. First they are collected as to original penetration design. Within each design they are collected according to each sub-fraction. Also, within each sub-fraction they are organized according to road quality with the best quality road first.

Interpretation of each graph should be done by recalling from the main text that the high molecular size materials occur at the far right and light ends occur at far left. The graphs at the far left end beyond 40 show very small molecules such as water, heptane and a number of inconsequential molecules. Data beyond 40 were not included in the main text because these adulterants probably arise from the analysis process itself.

Abbreviations are:

WA - Whole Asphalt

ASP - Asphaltenes

HA - Heavy Aromatics

LA - Light Aromatics

SAT - Saturates

PLEASE NOTE: FULL SET OF 63 CHROMATOGRAMS FOR THIS STUDY AVAILABLE UPON REQUEST FROM THE PLANNING AND RESEARCH BUREAU, MONTANA DEPARTMENT OF HIGHWAYS, 2701 PROSPECT AVENUE, HELENA, MONTANA 59620.

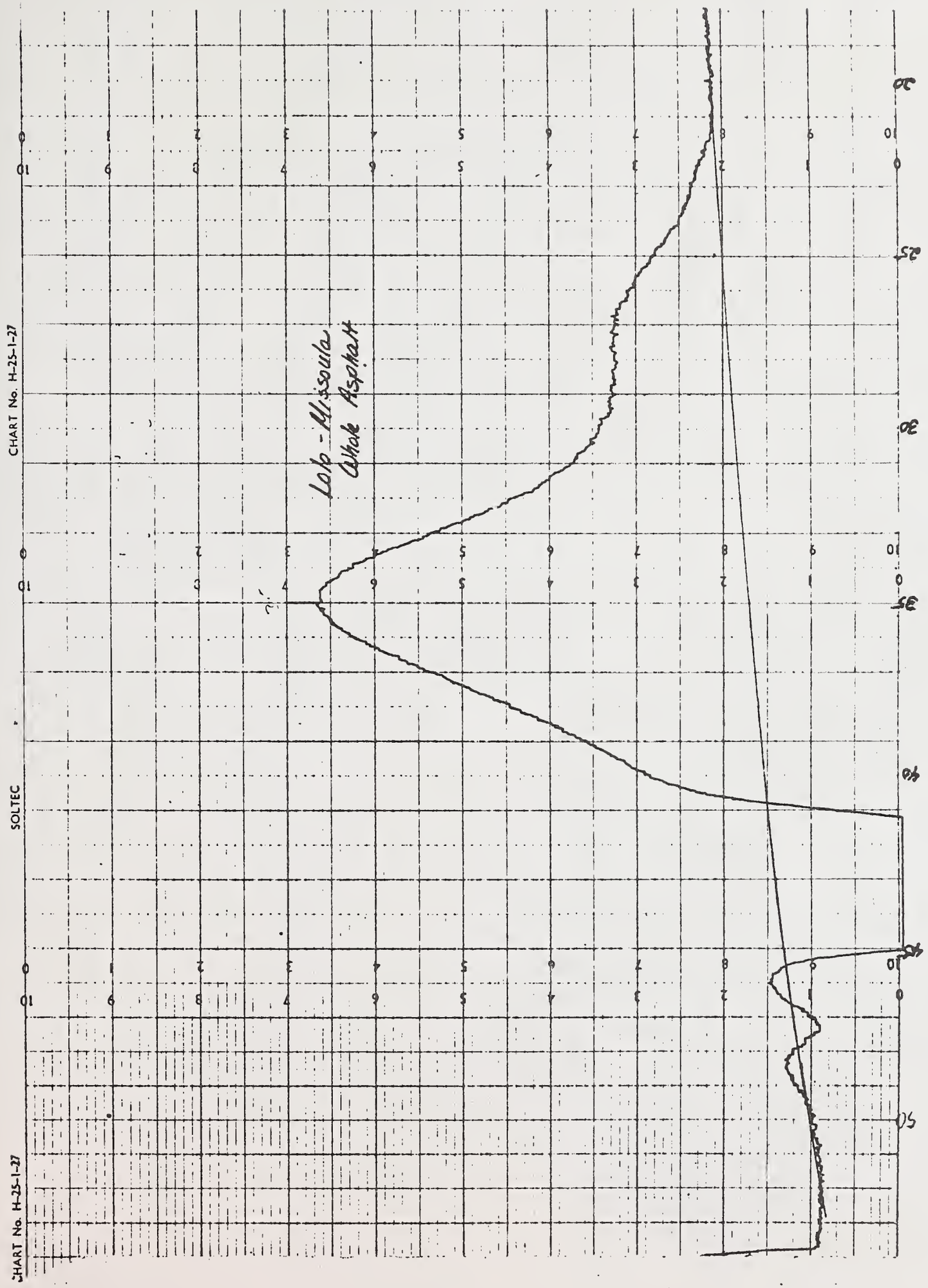
CHART No. H-25-1-27
SOLTEC
Lolo - Missoula
Chart Asphalt
CHART No. H-25-1-27

FIGURE 17